

# ON THE FLUORESCENCE OF PARACHLOROTOLUENE IN THE SOLID STATE AT LOW TEMPERATURE\*

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## Plate IV

**ABSTRACT.** The fluorescence spectra of pure *p*-chlorotoluene in the solid state at  $-30^{\circ}\text{C}$  and  $-180^{\circ}\text{C}$  have been investigated using filtered Hg radiation and the spectrum has been compared with those due to frozen solutions of the substance in benzene, *n*-heptane, methyl cyclohexane, methyl alcohol, carbon tetrachloride, tetrachloroethylene and carbon disulphide of different concentrations. Altogether eight bands are produced by the pure substance and these diminish in intensity abruptly as the temperature of the solidified mass is raised from  $-180^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$ . The bands persist with undiminished intensity even in the case of a 2% solution of the substance in benzene, carbon tetrachloride and tetrachloroethylene at  $-180^{\circ}\text{C}$ . In the case of solution in methyl cyclohexane, *n*-heptane and methyl alcohol at  $-180^{\circ}\text{C}$ , strong new bands appear in the fluorescence spectra. When the substance is dissolved in carbon disulphide and the solution is frozen and cooled to  $-180^{\circ}\text{C}$ , the bands persist upto 15% concentration, but the intensities of the bands diminish rapidly and the bands almost disappear as the concentration is reduced to 5%. The results have been explained on the assumption that the formation of virtual links between the chlorine and hydrogen atoms of the *p*-chlorotoluene molecule respectively with hydrogen and chlorine atoms of the neighbouring molecules in the solidified mass is responsible for the production of the metastable states giving rise to the observed fluorescence. It is pointed out that the absence of fluorescence in very dilute frozen solutions in carbon disulphide corroborates this hypothesis.

## INTRODUCTION

While studying the Raman spectra of ortho- and para-chlorotoluene at low temperatures, Sanyal (1953) first observed that either of these two compounds produces fluorescence in the visible region in the solid state at  $-180^{\circ}\text{C}$ . Later, the present author (Biswas, 1954, 1955a, 1955b) observed that many substituted benzene compounds give rise to similar fluorescence in the visible region when the substances are solidified and cooled down to  $-180^{\circ}\text{C}$ . The experimental arrangements in these cases were not, however, suitable for studying the fluorescence spectra at low temperatures, as the mercury lines in the near ultraviolet region were largely absorbed by the glass condensers used in these experiments and also other mercury lines were overexposed. The fluorescence

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bands reported by these authors were therefore, probably incomplete. It would be of interest to find out the complete spectrum and the influence of environment on it, because such data might throw some light on the origin of these fluorescence spectra. The investigation of the fluorescence of some frozen substituted benzenes was, therefore, undertaken and the results obtained in the case of *p*-chlorotoluene are discussed in the present paper.

#### EXPERIMENTAL

Para chlorotoluene used in the present investigation was supplied by Eastman Kodak Co., N.Y. and it was of chemically pure quality. The liquid was again repeatedly fractionated in vacuum before exposure. The purity was also tested by studying the Raman spectrum of the liquid and it was observed that there were no extra feeble Raman lines and the background was clear.

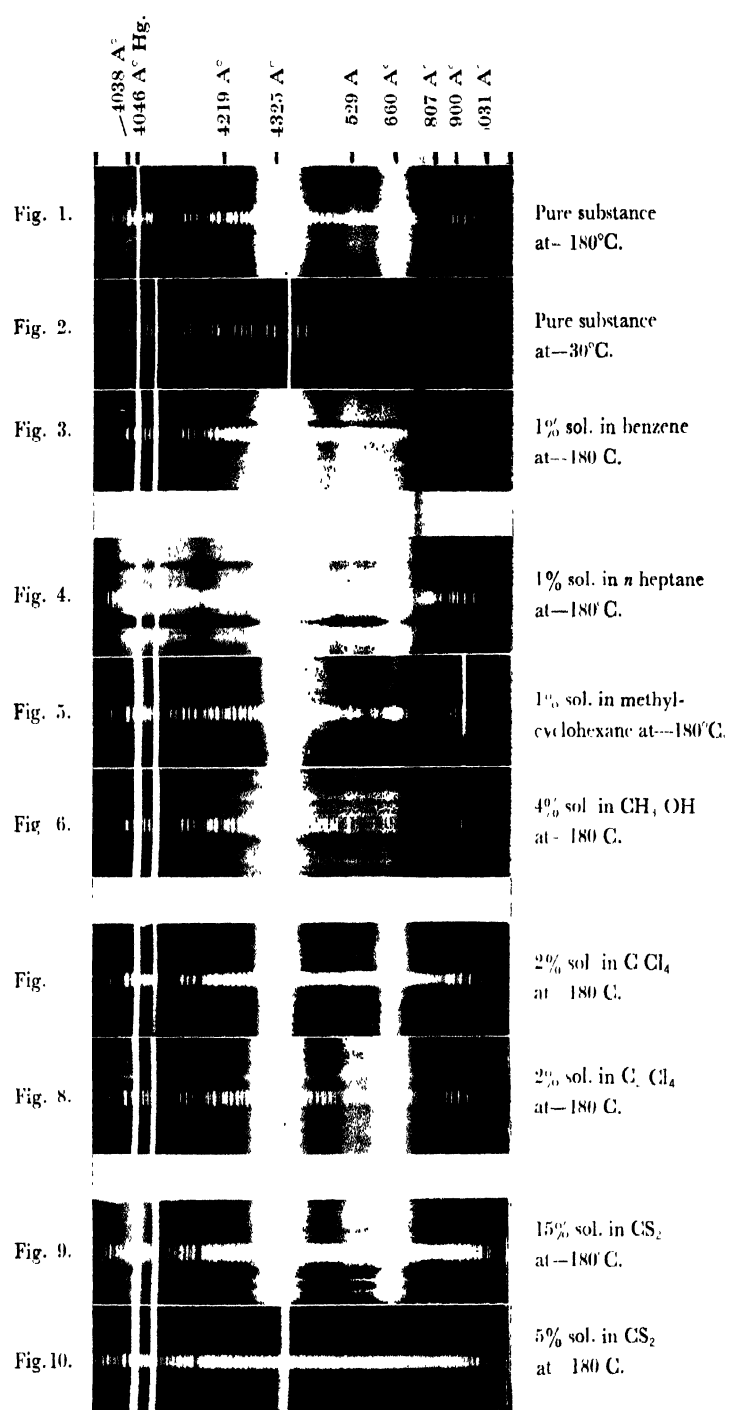
The incident beam, which is generally used for illuminating the sample in studying Raman spectra at low temperature, was slightly modified in the present case. A light filter transmitting the 3600 Å group of Hg-lines and almost cutting off the other mercury lines of longer wavelengths was placed in the path of the incident light from a mercury arc. It was observed in the preliminary investigation that after the introduction of this filter it becomes practically immaterial whether we use containers of fused silica or of pyrex glass. So, pyrex glass containers were used in the final investigation. The samples were solidified by dipping the container in liquid oxygen. Besides the fluorescence spectra of the frozen liquid at different low temperatures those of the solutions of the substance in benzene, *n*-heptane, methyl cyclohexane, carbon tetrachloride, tetrachloroethylene and carbon disulphide of concentrations varying from 15% to 1% were also investigated. All these solutions of strengths below 10% appear as homogeneous solid mass when frozen by liquid oxygen and the mass is almost transparent throughout its entire volume.

The spectra were photographed on Ilford Zenith plates using a Fuess glass spectrograph of dispersion about 11 Å in the 4046 Å region. On each spectrogram an iron arc spectrum was superposed for comparison.

As the bands were observed to be very broad a slit width varying from 0.3 to 0.6 mm. was used to reduce the time of exposure.

#### RESULTS AND DISCUSSION

The positions, approximate widths, estimated relative intensities and the successive distances of the fluorescence bands exhibited by pure *p*-chlorotoluene in the solid state at  $-180^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$  and those due to a 1% solution in benzene at  $-180^{\circ}\text{C}$  are given in Table I. The relative intensities are indicated as very strong (v.s), strong (s) etc., in the tables. The spectra due to 5% and

Fluorescence spectra of *p*-chlorotoluene.

10% solutions in benzene were found to be practically identical with that of the 1% solution.

The fluorescence bands given by 1% solutions of *p*-chlorotoluene in *n*-heptane and in methyl cyclohexane and also the bands given by a 4% solution in methyl alcohol cooled down to  $-180^{\circ}\text{C}$  are similarly shown in Table II. A 5% solution of the substance in *n*-heptane also gives the same spectrum as the 1% solution.

Similar data for 2% solutions of *p*-chlorotoluene in carbon tetrachloride and tetrachloroethylene are given in Table III. A 5% solution of this substance in  $\text{CCl}_4$  gave exactly the same spectrum as the 2% solution. The fluorescence bands due to a 15% and a 5% solution of *p*-chlorotoluene in carbon disulphide are given in Table IV. Some of the spectrograms are reproduced in Plate IV.

TABLE I:  
Fluorescence spectra

Substance	Position of the band in A.U.	Width of the band in A.U.	Position of the band in $\text{cm}^{-1}$	Successive differences in $\text{cm}^{-1}$
<i>p</i> -Chlorotoluene at $-30^{\circ}\text{C}$ .	4325 (w)	106	23115	1662
	4660 (w)	80	21453	
	4038 (s)	77	24758	1062
	4219 (m)	80	23696	
	4325 (v.s.)	122	23115	
<i>p</i> -Chlorotoluene at $-180^{\circ}\text{C}$ .	4529 (s)	81	22074	1041
	4660 (v.s.)	120	21453	621
	4807 (v.w.)	35	20797	656
	4900 (w)	60	20402	395
	5031 (v.w.)	38	19871	531
	4048 (m)	100	24697	1001
	4219 (s)	85	23696	
	4307 (v.s.)	70	23212	484
1% solution of <i>p</i> -chlorotoluene in benzene at $-180^{\circ}\text{C}$ .	4362 (m)	64	22919	293
	4529 (s)	80	22074	845
	4660 (s)	135	21453	621
	4800 (w)	—	20827	626

TABLE II  
Fluorescence spectra

Substance (frozen and cooled down to $-180^{\circ}\text{C}$ )	Position of the band in A.U.	Width in A.U.	Position of the band in $\text{cm}^{-1}$	Successive differences in $\text{cm}^{-1}$
1% solution of <i>p</i> -chlorotoluene in <i>n</i> -heptane	4025 (s)	83	24838	643
	4132 (m)	44	24195	499
	4219 (m)	80	23696	533
	4316 (v.s.)	91	23163	642
	4439 (s)	34	22521	447
	4529 (m)	75	22074	621
	4660 (v.s.)	124	21453	656
	4807 (w)	37	20797	395
	4900 (?)	—	20402	531
	5031 (w)	38	19871	
1% solution of <i>p</i> -chlorotoluene in methyl cyclohexane	4032 (m)	59	24795	665
	4143 (m)	28	24130	434
	4219 (m)	90	23696	581
	4325 (s)	85	23115	670
	4454 (m)	19	22445	371
	4529 (w)	50	22074	653
	4667 (s)	24	21421	205
	4712 (m)	87	21216	462
	4817 (m)	51	20754	918
	5040 (v.w.)	45	19836	
4% solution of <i>p</i> -chlorotoluene in methyl alcohol	4030 (m)	28	24807	671
	4142 (w)	25	24136	254
	4186 (w)	27	23882	192
	4220 (v.w.)?	—	23690	294
	4273 (m)	15	23396	270
	4323 (s)	30	23126	436
	4406 (m)	36	22690	616
	4529 (m)	40	22074	621
	4660 (s)	142	21453	626
	4800 (w)	35	20827	

TABLE III

## Fluorescence spectra

Substance (frozen and cooled down to $-180^{\circ}\text{C}$ )	Position of the band in A.U.	Width in A.U.	Position of the band in $\text{cm}^{-1}$	Successive differences in $\text{cm}^{-1}$
2% solution of <i>p</i> -chlorotoluene in carbon tetrachloride	4038 (m)	77	24758	
	4219 (w)	80	23696	1062
	4325 (v.s.)	122	23115	581
	4529 (m)	81	22074	1041
	4660 (v.s.)	120	21453	621
	4900 (v.w)	53	20402	1051
	5031 (v.w)	35	19871	531
2% solution of <i>p</i> -chlorotoluene in tetrachloroethylene	4038 (w)	70	24758	
	4219 (w)	74	23696	1062
	4325 (v.s)	120	23115	581
	4529 (m)	75	22074	1041
	4660 (s)	116	21453	621
	4807 (v.w)	—	20797	656
	5031 (v.w)	35	19871	926

TABLE IV

## Fluorescence spectra

Substance (frozen and cooled to $-180^{\circ}\text{C}$ )	Position of the band in A.U.	Width in A.U.	Position of the band in $\text{cm}^{-1}$	Successive differences in $\text{cm}^{-1}$
15% solution of <i>p</i> -chlorotoluene in carbon disulphide	4038 (m)	70	24758	
	4219 (m)	72	23696	1062
	4325 (v.s)	116	23115	581
	4529 (s)	75	22074	1041
	4660 (v.s)	118	21453	621
	4807 (v.w)?	—	20797	656
	4900 (v.w)	—	20402	395
5% solution of <i>p</i> -chlorotoluene in carbon disulphide	5031 (v.w)	32	19871	531
	4325 (v.w)		23115	
	4660 (v.w)		21453	1662

It is found from Table I that when the solidified mass of *p*-chlorotoluene is cooled down to  $-30^{\circ}\text{C}$  only two weak fluorescence bands are observed at 4325 and 4660 Å respectively. When the temperature of the solid is lowered to  $-180^{\circ}\text{C}$ , the intensity of fluorescence increases enormously and besides the two bands mentioned above six more weaker bands are observed. Table I further shows that when the substance is dispersed in frozen benzene the fluorescence bands undergo some changes. The bands at 4219 and 4529 Å become stronger while the broad band at 4325 Å appears to be split up into two components at 4307 and 4362 Å respectively. The three weaker bands at 4807, 4900 and 5031 Å seem to merge into one another to form a broad and weak band at 4800 Å.

Table II shows that the fluorescence spectrum is altered appreciably if the substance is dispersed in frozen *n*-heptane, methyl cyclohexane or methyl alcohol, the change depending on the nature of the solvents. In the case of the solution of *n*-heptane each of the strong bands at 4038 and 4325 Å splits up into pairs at 4025 and 4132 Å, 4316 and 4439 Å respectively. The wave number difference between the components in each pair is about  $642\text{ cm}^{-1}$ . Further, the band at 4807 Å seems to become stronger and that at 4900 Å becomes weaker when the substance is dispersed in frozen *n*-heptane. In the case of solution in methyl cyclohexane also each of the three strong bands breaks up into two components which are at 4032 and 4143 Å, at 4325 and 4454 Å and at 4667 and 4712 Å respectively while the band at 4807 Å shifts to 4817 Å and becomes stronger. In the case of the solution in methyl alcohol either of the bands at 4038 and 4219 Å breaks up into a pair of components while the strong band at 4325 splits up into three components at 4273, 4325 and 4406 Å respectively. Amongst the three weak bands on the longer wavelength side, only one diffuse band can be observed at 4800 Å in this case.

Table III on the other hand shows that when the molecules of *p*-chlorotoluene are dispersed in carbon tetrachloride or tetrachloroethylene in the solid state the fluorescence spectrum is only slightly altered. In the former case the band at 4807 Å disappears and in the latter case the relative intensities of some of the bands undergo slight changes.

Table IV shows that the nature of the fluorescence spectrum is not at all altered when *p*-chlorotoluene is dissolved in carbon disulphide, but the intensity of fluorescence diminishes rapidly with lowering of concentration of *p*-chlorotoluene in carbon disulphide. The fluorescence spectrum is observed to be intense in the case of a 15% solution of *p*-chlorotoluene in carbon disulphide,

but the fluorescence tends to disappear when the strength of the solution is reduced from 15% to 5% by volume.

The appearance of fluorescence in *p*-chlorotoluene in the solid state at low temperature and also the rapid increase in its intensity with lowering of temperature of the solidified mass suggest that the fluorescence is due to the influence of intermolecular field which seems to increase rapidly with lowering of temperature. In order to understand whether this intermolecular field is to be identified with the lattice field of the crystalline substance or it is due to the formation of small groups of associated molecules, the fluorescence spectra of the substance in dilute solutions in a number of solvents are to be examined carefully. The results given in Tables I—III show that the fluorescence persists even in very dilute solutions of the substance in benzene, *n*-heptane, methyl cyclohexane, methyl alcohol, carbon tetrachloride and tetrachloroethylene. When *p*-chlorotoluene is dissolved in small quantities in these solvents and the solutions are frozen, the molecules remain dispersed homogeneously in the frozen mass and the solute does not separate out in the form of small crystals. Further, to prevent the fluorescence coming out from any such separated crystallites from entering into the spectrograph, fluorescence from the upper portions of the frozen solutions was studied in the case of solvents lighter than the substance and in the case of heavier solvents the lower portions of the solidified solution were used, so that there was very little chance for the fluorescence of such separated crystals to fall on the slit of the spectrograph. Hence the fluorescence exhibited by the frozen solutions cannot be due to lattice field in the pure substance. It appears, therefore, that when the molecules of *p*-chlorotoluene come very close to each other, they probably form small groups amongst themselves and the distortion produced in the molecules in these groups in the solid state at low temperature leads to the production of metastable states responsible for this fluorescence.

It is observed that different solvents have different influence on the fluorescence spectrum of this substance. The influence is the least in the case of benzene used as the solvent, but the other aliphatic solvents alter the spectra appreciably.

These results can be interpreted on the following assumptions. In the case of the pure substance in the solid state whenever virtual bond is formed between the chlorine atom of one *p*-chlorotoluene molecule and the hydrogen atom of a neighbouring molecule, the metastable states are produced. When the molecules are dispersed in benzene, the chlorine atom of the *p*-chlorotoluene molecule probably forms such virtual bond with the hydrogen atom of a neighbouring benzene molecule and again almost the same metastable state is produced. So even in the case of 1% solution the fluorescence persists without diminution in intensity. When the aliphatic solvents are used, the chlorine atom of the *p*-chlorotoluene atom again forms virtual bonds with the hydrogen atoms



of the  $\text{CH}_2$  groups, but the metastable states produced in this way are different from those produced by similar attachment of the chlorine atom to the hydrogen atom of the benzene ring. Hence the fluorescence persists with undiminished intensity even in the case of 1% solutions although the spectrum is altered appreciably. When the solvent molecule does not contain any hydrogen atom but contains chlorine atoms, the hydrogen atoms of the *p*-chlorotoluene molecule can be attached to the chlorine atoms of the neighbouring solvent molecules and even then nearly the same metastable states are produced as in the case of the pure substance. It appears that the bands at  $4325 \text{ \AA}$  and  $4660 \text{ \AA}$  are due to such attachment of the chlorine atom of the solvent molecule to the ring of the *p*-chlorotoluene molecule while the bands at  $4038 \text{ \AA}$  and  $4529 \text{ \AA}$  are produced by attachment of hydrogen atom of the solvent molecule to the chlorine atom of the *p*-chlorotoluene molecule because these latter two bands become weaker when the substance is dispersed in solidified  $\text{C}_2\text{Cl}_4$ .

The results obtained using carbon disulphide as the solvent seem to support the assumption mentioned above. It has been observed that the fluorescence persists in the case of 15% solution of the substance in frozen  $\text{CS}_2$ , but it almost disappears abruptly when the concentration is reduced to 5%. The times of exposure and the width of the slit of the spectrograph were suitably adjusted to verify this conclusion. Also, the spectrum of the light coming only from the lower portion of the frozen solution was recorded. It appears that in the case of the 15% solution some of the molecules of *p*-chlorotoluene exist as dimers or in small associated groups giving rise to the metastable state, while such groups break up into monomers at lower concentrations.

It can be clearly seen that the abrupt disappearance of the fluorescence with the change of concentration from 15% to 5% can not be due to the quenching by  $\text{CS}_2$  molecules, because if a quenching effect would exist, no fluorescence could be observed in the case of the 15% solution. Further, the fluorescence spectrum is in the visible region while the longest electronic absorption band of the  $\text{CS}_2$  molecule lies in the region between  $3400 \text{ \AA}$ – $800 \text{ \AA}$ , and therefore, the fluorescence cannot be quenched by carbon disulphide molecules.

The results thus furnish new evidence for the formation of strongly associated groups of molecules in the solid state of such substituted benzene molecules. Investigations with other compounds are in progress.

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## *Letter to the Editor*

### THE ULTRAVIOLET ABSORPTION SPECTRUM OF META-FLUOROCHLOROBENZENE

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In continuation of the work on the ortho-fluoro-chlorobenzene (author, 1955), the ultraviolet absorption spectrum of meta-fluorochlorobenzene in the vapour state was studied, the only previous investigation on the absorption of this molecule being in hexane solution by Conrad-Hillroth (1936). The spectrum was photographed with path lengths 15, 50 and 75 cms and at different temperatures ranging from  $-80^{\circ}\text{C}$  to about  $+100^{\circ}\text{C}$ .

Two regions of absorption were observed :

(1) a continuous one below  $2150 \text{ \AA}$  and (2) a discrete one in the region  $2850\text{--}2350 \text{ \AA}$ . These two regions merge together at higher vapour pressures. The bands in the discrete region are red degraded and about 200 of them were measured. This system could be interpreted as due to the electronic transition  $A'-A'$ . In accordance with this a strong 0,0 band and progressions and combinations of many totally symmetrical vibrations were observed. The strong band at  $37026.5 \text{ cm}^{-1}$  was chosen as the 0,0 band of the system. Most of the bands were interpreted in terms of five upper state and four lower state frequencies. These, together with other data, are presented in Table I.

TABLE I

Ground and excited state frequencies of  $m\text{-C}_6\text{H}_4\text{F.Cl}$

Raman data (Kohlrausch, 1935)		U.V. absorption data		Tentative assignment
	Int.	Ground state	Excited state	
683	7	688	636 (st)	C-Cl stretching
880	2	895	846 (m)	
1002	10	1007	966 (vst)	Carbon ring breathing
1060	4	..	1023 (s)	
1217	4	1229	1218 (ms)	C-F stretching

On the red side of each of the strong bands, satellite bands were observed with frequency separations of 42 and 78  $\text{cm}^{-1}$ , the latter being more pronounced. These bands were interpreted as the  $v-v$  transitions of some of the low lying vibrations. All strong bands also exhibit a double-headed structure with a separation of 6  $\text{cm}^{-1}$ . These double heads are most probably rotational fine structure. A portion of the spectrum is reproduced in figure 1.

A detailed discussion of the analysis will be published shortly.



Fig. 1. Part of the U.V. absorption spectrum of *m*-fluorochlorobenzene

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